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R.163/34/April 1969

HEATS OF FORMATION OF
LIGHT ELEMENT COMPOUNDS

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Contract AF 61(052)-863

28 April 1969

PROGRESS REPORT No. 16

HEATS OF FORMATION OF LIGHT ELEMENT COMPOUNDS

1 JANUARY 1969 - 31 MARCH 1969

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R.163/34/April 1969

This research has been sponsored in part by the AIR FORCE OFFICE
OF SCIENTIFIC RESEARCH through the EUROPEAN OFFICE OF AEROSPACE
RESEARCH, OAR, UNITED STATES AIR FORCE, under Contract Number
AF 61(052)-863

HEATS OF FORMATION OF LIGHT ELEMENT COMPOUNDS

1. SUMMARY OF THE WORK ACCOMPLISHED

A. Heats of formation of iodides by direct reaction of an element with iodine

Two sets of experiments have been made, one in which the element was reacted with liquid iodine at about 120°C, the other in which it was reacted with iodine vapour at 240-260°C at saturation pressure at approximately 4 atmospheres.

(a) Reaction with liquid iodine

The arrangement used was similar to that employed in the determination of the heat of formation of titanium bromide by reaction with liquid bromine in entirely closed glass vessels⁽¹⁾. Pure aluminium turnings react completely with liquid iodine, no free aluminium being found after the reaction. Similarly, titanium pieces react completely. However, crystals of Pechiney beryllium under the same conditions remain mostly unreacted.

(b) Reaction with iodine vapour

Since it has been found previously that metals (columbium, tantalum) do not react with liquid bromine but can be brought to reaction with bromine vapour at ~4 atm when kindled with titanium⁽²⁾, experiments similar to those used in the determination of the heat of formation of columbium and tantalum bromide in glass vessels were made. A titanium piece, when reaction was initiated by a smaller piece of the same material above it, reacted to completion with iodine vapour. Similarly, aluminium reacted completely with the vapour. However, when a beryllium rod was placed in the reaction vessel and a titanium sleeve mounted on it for ignition, the beryllium rod did not react. Since it was thought possible that a thin layer of beryllium oxide on the rod prevents reaction, the rod was washed in dilute hydrochloric acid and an aluminium sleeve mounted on it for ignition. The beryllium rod, however, did not burn. Similarly,

a beryllium rod on to which an aluminium wire was wound and which carried a magnesium ribbon for triggering off the reaction, also did not burn.

Finally, a briquette of 60 atomic per cent aluminium powder and 40 per cent amorphous boron was made and an aluminium kindler attached to it. The aluminium of the initiator burnt to completion but the briquette remained mostly unchanged

D. Beryllium boride

Three sets of different types of experiments for the determination of the heat of formation of beryllium boride were made.

(a) The experiments of heating beryllium boride in a stream of chlorine mentioned in the last Progress Report No. 15 have been continued. It has been noticed that, probably because of violent gas evolution at the start of the chlorination experiments, part of the very light beryllium boride powder was blown out of the crucible into the cooler part of the set-up and thereby escaped reaction. Experiments were therefore made in which the chlorine was diluted with argon in various proportions, Ar/Cl_2 from $3/8$ to $1/4$. In general the reaction was incomplete, but complete reaction could be achieved in a stream of argon + chlorine ($\text{Ar}/\text{Cl}_2 = 3/8$); however, the energy input to the furnace in the calorimeter was too high, corresponding to about 2°C temperature rise, for successful operation.

The chlorination experiments were discontinued because of the incomplete combustion and because recourse to analysis of the reaction product or the residue appears of doubtful value. The residues were not soluble in dilute hydrochloric acid, and it is assumed that they consist of a boride different from Be_2B .

(b) The application of a method previously used successfully in the determination of the heat of formation of various uranium silicides⁽³⁾ was investigated. In these experiments the heat of reaction between beryllium boride powder with an excess of tellurium would be compared with the heat of reaction of the same amount of a stoichiometric mixture

of beryllium and boron with the same excess of tellurium. The reaction mixture is heated in the small furnace within the calorimeter. In the first of these experiments with beryllium boride heating the reaction mixture for 10 minutes up to 650-675°C, a heat evolution of 150 cal was observed, which corresponds to only 10 per cent of that which one would expect. The heat of reaction of a stoichiometric mixture of beryllium and boron with tellurium was even smaller. In a further experiment the compound plus tellurium was heated to 850°C with a heat evolution of 480 cal which appears still too small and on re-heating, again to 850°C, another 162 cal were evolved.

Stoichiometric mixtures of $2\text{Be} + \text{B} + 7\text{Te}$ were heated to 800°C with a heat evolution of only 300 cal. When the mixture was re-heated to 900°C a further 150 cal were evolved. These heats are too small and represent incomplete reaction; the difficulty of bringing about complete reaction is ascribed to a protective oxide layer on the surfaces of beryllium metal and of the boride. The surface layer may possibly be broken down if the reaction mixtures were compressed to briquettes but the use of briquettes needs a modification of design and handling of the apparatus which has not yet been evolved.

(c) Since the protection by a very thin oxide layer would be overcome by the use of a reactant which eliminates the oxide layer, experiments were carried out in which beryllium boride was dissolved in hydrochloric acid containing an oxidizing agent to prevent the evolution of hydrogen and particularly boron hydride. Closed glass vessels similar to those employed in the determination of the heats of formation of the carbides of beryllium and aluminium⁽⁴⁾ have been used. Such experiments could be combined with comparison experiments on the heat of solution of metallic beryllium and anhydrous boric acid, with suitable corrections. Various experiments using bromine-bromide solution and hydrochloric acid have been carried out at various temperatures. About 100 mg of beryllium boride could be dissolved in solutions, 5N HCl, 1.5N bromine and 1.0N KBr, but it took 2 hours at 50°C to achieve complete dissolution. There was

a slight gas evolution which consisted however of only 2 per cent of the maximum hydrogen evolution possible. The gas was subsequently diffused through a palladium tube and only very minute amounts of boron could be detected on the palladium. Correction for the 2 per cent hydrogen evolution could be relatively easily made but the duration of 2 hours is considered too long for precise measurements.

The temperature of reaction was therefore increased to 110°C, using 2.5N HCl, 1.5N Br₂ and 2N KBr. Complete dissolution occurred under these conditions in a few minutes but the hydrogen evolution was much higher amounting to approximately 30 per cent of the maximum possible. Experiments using an intermediate temperature and higher concentrations of free bromine are in progress but have not yet been fully analysed.

C. Equilibrium between beryllium dichloride, lower beryllium chloride and beryllium

Since the experiments have been carried out in an alumina effusion cell, the possibility of reaction of beryllium metal with the alumina and subsequent distillation of aluminium as monochloride (and free metal) exists. Aluminium in the vapour phase would be absorbed on the nickel or platinum absorber. Most of the plates from the spectrographic determination of the beryllium in the absorber have been re-examined for aluminium and appropriate very small corrections have been made. This work delayed finalising the Scientific Report

D. Mixed Oxides

Progress has been made with the compilation of a comprehensive Scientific Report which, however, is not yet complete.

2. WORK IN THE NEXT PERIOD

A. Reaction of elements with iodine

The possibility of reacting elements with iodine at elevated temperatures will be considered.

B. Beryllium boride

The dissolution of beryllium boride in closed glass vessels in hydrochloric acid-bromine or another oxidising agent will be continued.

C. Equilibrium between beryllium dichloride, lower beryllium chloride and beryllium

A Scientific Report will be issued.

D. Mixed Oxides

A Scientific Report in one or two parts will be issued.

3. Mr. G. C. Curme, B.Sc., has joined the team.
4. No inventions were conceived or made during the reporting period.

PG/JMN
28.4.1969

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